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Freeze-casting to create micro-channels in $La_{0.66}Ca_{0.33-x}Sr_xMn_{1.05}O_3$

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Introduction

The templating technique of freeze casting is utilized as a way of creating directional porosity in the form of micro-channels in $La_{0.66}Ca_{0.33-x}Sr_xMn_{1.05}O_3$ (LCSM). LCSM is a magnetocaloric material in which the Curie temperature can be controlled by varying strontium doping (x), making it ideal for application as regenerator-material in magnetic refrigeration [1]. One way to increase the cooling performance of a magnetic regenerator is by optimizing its geometry; while maintaining a large surface area to increase heat exchange with the regenerator fluid, it must not provide too much resistance to flow. It has been proposed that a matrix of micro-channels with a width of 100 µm is an optimum geometry [2].

Freeze-casting results in channels of widths of 10 to 100 µm, where the porosity depends on the solid load while the size and homogeneity of the channels depends on freezing conditions [3][4].

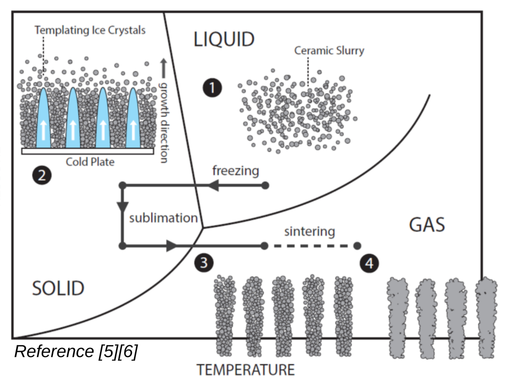
The figure on the right shows solid magnetic regenerators made of magnetocaloric materials of packed irregular particles and stacked plate geometries. A geometry in between – such as a micro-channel matrix – would be optimum.

Objectives

- Fabrication of LCSM ceramics with micro-channels by freeze casting
- Increase homogeneity of channels along the height of the sample by implementing dynamic freezing profiles instead of static freezing profiles
- Alter morphology of channels by gelation freeze casting, i.e. using gelatin to create a stable gel suspension before the freezing step

Background

In freeze casting, a ceramic aqueous suspension (1) is directionally frozen (2). The ice crystals are removed by sublimation (3) leaving directional voids or channels in the material which is then sintered to a solid (4).



Experimental set-up

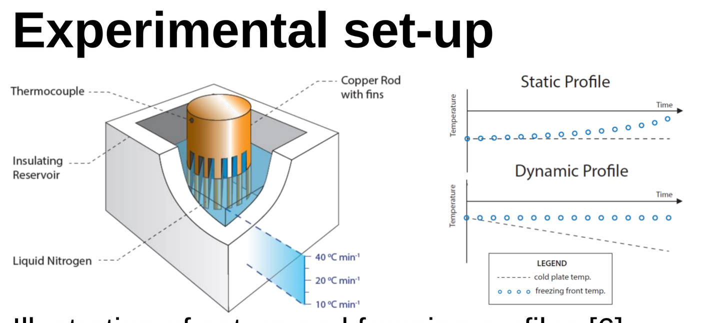


Illustration of set-up and freezing profiles [6].

Materials and methods

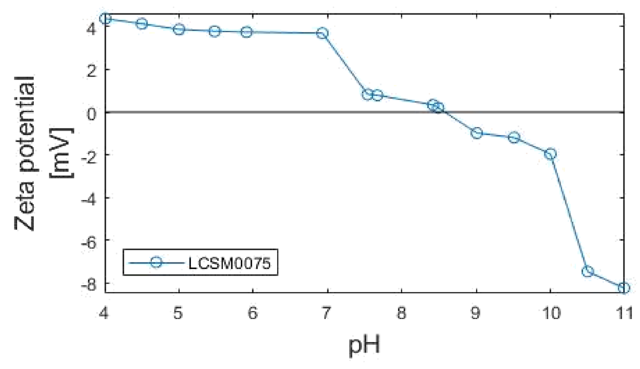
The standard freeze casting route is altered in two steps:

Dynamic and static freezing: Samples were frozen either statically at –96° or dynamically at –10 °C/min.

Gelation freeze casting: Gelatin was added at 0.3 wt% (of solids) and left to harden before freezing

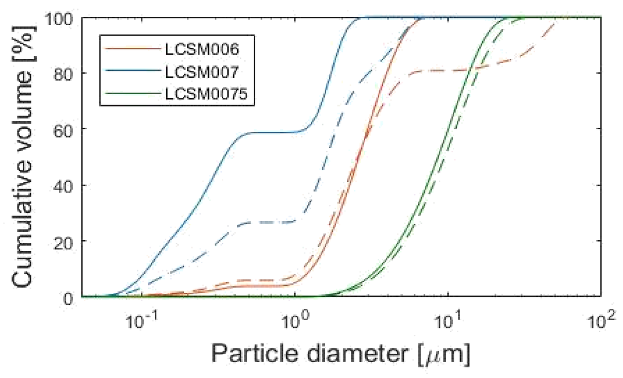
Powders were used as received from Cer-Po-Tech and characterized as follows:

	x	Density [g/cm^3]	Surface area [m^2/g]	d_{50} [µm]	Isoelectric point
LCSM006	0.06	6.0011	10.12	2.598	-
LCSM007	0.07	6.0401	17.92	0.343	8.79
LCSM0075	0.075	6.0653	9.519	8.552	8.54

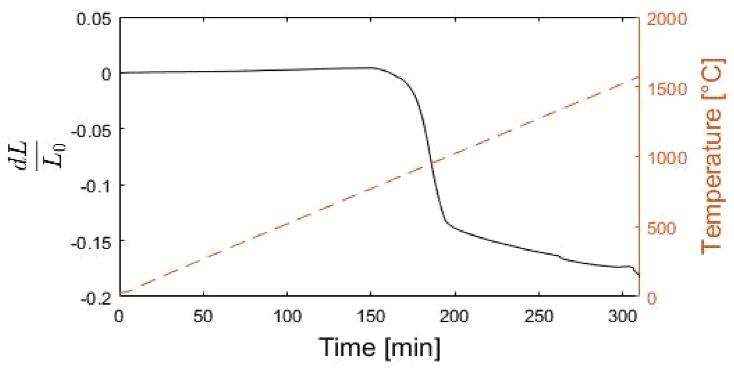


Measurements of Zeta potential as a function of pH for LCSM in a 1 wt% aqueous suspension.

The Zeta potential reaches a plateau at the lower pH range, indicating that a stable slurry is achieved at pH < 7. All slurries was thus prepared at pH ~ 6.



PSD of powders before and after 24h of low energy ball milling with dispersant indicated by dotted and solid lines respectively.

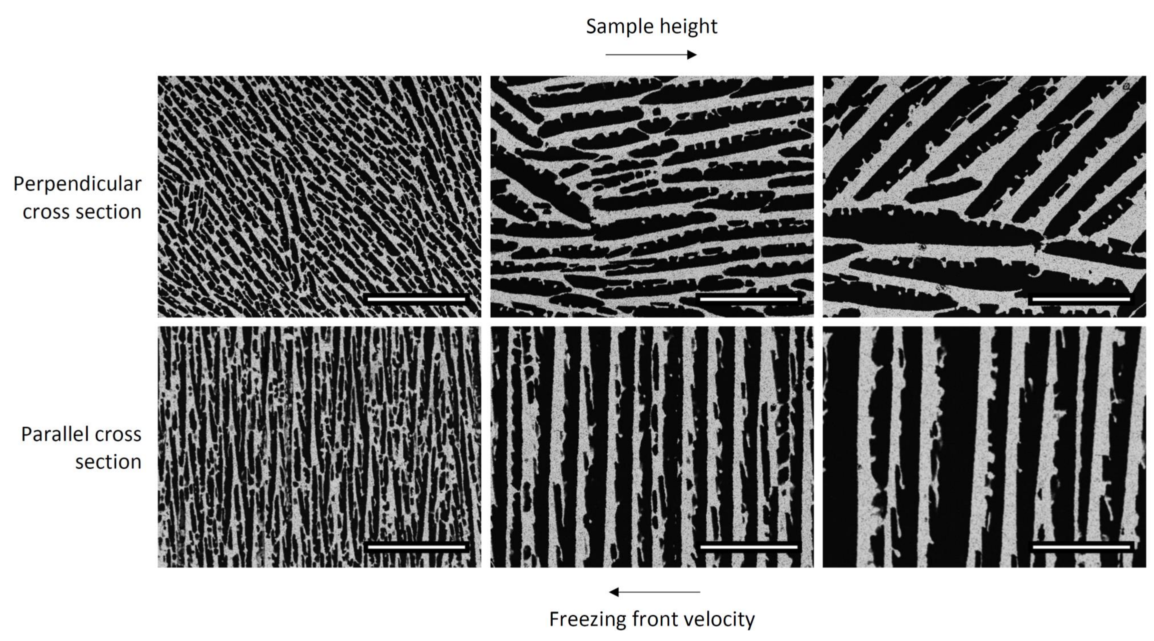


Slip casted sample sintered in a dilatometer at 5K/min.

LCSM starts densifying at 1000 °C. All samples were thus partially sintered at 1150 °C for 3h.

Results: Copper rod immersed directly in liquid N_2

Slurries of 14 vol% LCSM were freeze casted without control of temperature besides that of liquid N_2.

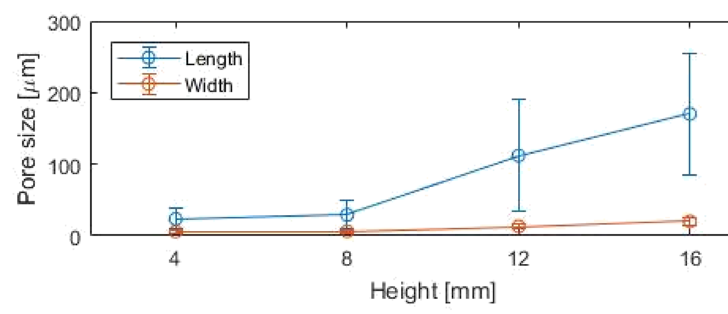


SEM images showing the cross section perpendicular and parallel to the freezing direction of 14 vol% LCSM006 frozen with no control of temperature.

Scale bar indicates 100 µm.

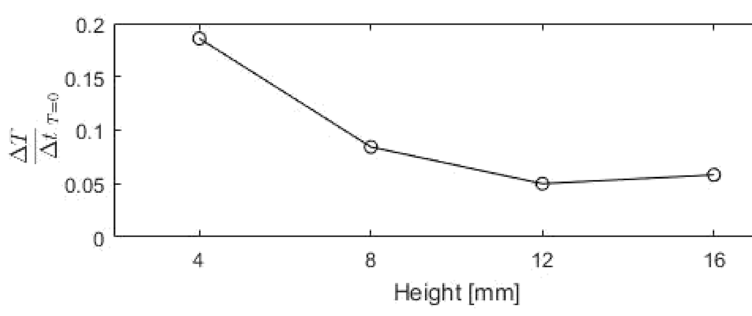
The freezing front velocity decreases as the ice height increases due to increased thermal resistance.

The lamellar pore size increases as the freezing front velocity decreases.



Length and width of lamellar pores were determined by fitting an ellipsoid to individual pores in ImageJ. Pore size is here plotted as a function of height.

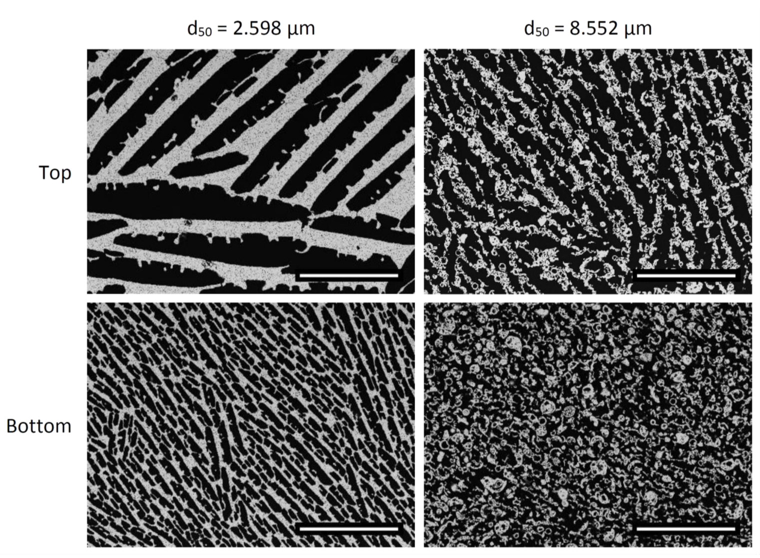
Lamellar pore width is increased by a factor of 3, while the length is increased by a factor of 7.



A continuous measurement of temperature in four locations along the sample height yields the temperature change with respect to time at the moment of freezing (T=0) plotted as a function of height.

The freezing driving force decreases along the height of the sample

Results: Varying particle size



SEM images showing the cross section perpendicular to the freezing direction of 14 vol% LCSM of varying particle size.

Scale bar indicates 100 µm.

Top: The wall thickness and particle size are in the same order of magnitude for the larger particles

Bottom: Larger and thus heavier particles are engulfed by the freezing front and no channels are formed.

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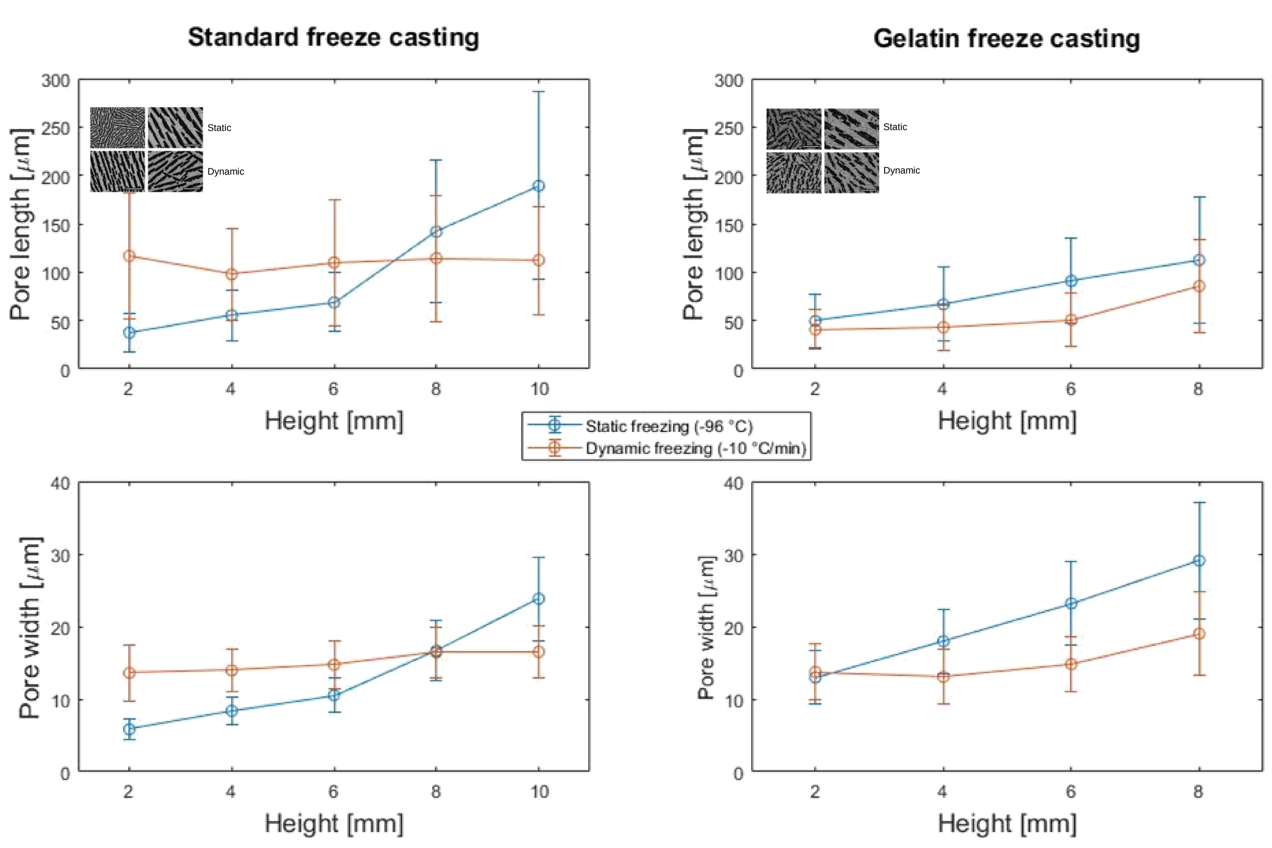
Results: Dynamic and static (gelation) freezing

Slurries of 20 vol% LCSM where freeze casted by dynamic and static freezing profiles, with and without the addition of gelatin.



Static freezing results in a large increase in both pore width and length along the height of the sample whereas the increase is much smaller for the dynamic freezing.

The aspect ratios in the gelation freeze casted samples are smaller than the samples without gelatin indicating more circular pores, possibly due to reduced R-crystal formation during ice growth.

Conclusions and outlook

Anisotropic porosity in the form of lamellar channels where achieved in LCSM ceramics with freeze casting, with increased homogeneity and lower aspect ratios achieved by implementing dynamic freezing profiles and an additional gelation step, respectively. Thus, future work includes:

- X-ray tomography to establish 3D structure (i.e. pore connectivity, quantification of gelation)
- Increased control of freezing for homogenous macrostructure
- Detailed quantification of microstructure to establish correlation between processing (specifically freezing and sintering) and structure
- Structure of ceramics vs. performance as regenerator material in magnetocaloric refrigeration systems

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